



Effect of aluminium oxide contaminants on the process of ozone decomposition in water

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ABSTRACT

In the recent years a number of publications have appeared on Al_2O_3 as ozonation catalyst. The results, however, raise many controversies. Adsorption of ozone on a surface of the catalyst and subsequent decomposition of O_3 molecule leading to formation of OH radicals is one of the possible mechanism of catalytic activity of alumina. However such the activity sometimes is observed while in other reports alumina does not show an ability to generate the radicals. As formation of the radicals depends strongly on pH controversial effects observed in the published papers may result from the lack of proper pH control. Aluminas are contaminated with alkali metals and the contaminants may cause unwanted (unexpected) changes in pH of ozonated solutions. The pH is a key factor responsible for the process of ozone decomposition in water. Therefore the purity of Al_2O_3 must be considered as an important parameter that can influence the process of ozone decomposition. This paper aims at showing that in the processes of catalytic ozonation special attention should be given to precise pH control. Commercially available aluminum oxides, purified by an extraction do not show the abilities to decompose ozone in water.

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1. Introduction

Catalytic ozonation is the area of science that has recently attracted a lot of attention and that results in numerous publications [1,2]. Aluminum oxide is one of the most often used catalyst or catalyst supports as its catalytic activity was shown in one of the first papers on catalytic ozonation [3]. However, many of the presented results may be considered controversial: in some papers catalytic activity was observed, [4–7], while in some reports alumina has not caused decomposition of ozone [8–10]. The controversies must have their reasons. There are three possible catalytic mechanisms in heterogeneous catalysis: i) ozone adsorbs on the catalyst surface and decomposes into the radicals, ii) organic compound adsorbs on the surface and adsorbed species are attacked by ozone molecules and iii) both ozone and organic molecules adsorb on the catalyst surface and react there. In this paper we discuss solely the first mechanism.

Decomposition of ozone in water strongly depends on pH. Therefore to assess the ability of a catalyst to decompose of ozone molecule it is absolutely necessary to compare ozone stability in water with and without catalyst at exactly the same Ph. However,

in many of the papers on catalytic properties of Al_2O_3 published to date not enough attention was paid to pH control [3,8,11,12], which is crucial particularly at high catalyst concentrations [13].

In the majority of published papers concerning the alumina as the catalyst there are no data on pH control not only after the catalyst introduction to the ozonated solution, but also during and after the completion of catalytic process. In the papers published to date pH value has been usually controlled at the beginning of the process (although in some papers [3,8] it was not controlled at all), and relatively rarely after the catalyst introduction and after the completion of the process. Controlling this parameter allows for the differentiation between the effect caused by pH increase and true catalytic effect.

Commercially available aluminum oxides are produced using the Bayer process, and then they are subjected to calcination in order to obtain the desired crystal phase [14]. Oxides produced in this way contain alkaline residues after the bauxite extraction as well as other contaminants remaining after the careless rinsing of ore. In most cases, available literature on the alumina as an ozonation catalyst either lacks information on the method of oxide purification or the data are scarce. It is therefore expected that alkaline contaminants of alumina may significantly change the pH of water after introduction of the catalyst to the ozonated solution. This paper aims at showing that mineral contaminants of aluminum oxide significantly affect the process of ozone decomposition because they are responsible for pH changes following the introduction of catalyst to water.

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2. Experimental

2.1. Materials and analytical methodology

Three commercially available aluminum oxides have been used in this study: activated aluminum oxide (AA – Nanning Elaiter Environmental Technologies Co. Ltd.), SAS 200 (SAS – BASF) and CDO Selexsorb® (CDO – BASF). The oxides have been used as unpurified and purified materials. The purification of oxides was conducted by: rinsing them first with 200 mL with HCl (0.1 M Chempur) and then with water to neutrality. Another portions of the oxides were extracted with high purity water (Millipore) in Soxhlet apparatus. Aqueous extracts used in the ozone decomposition experiments were obtained by 5 h continuous extraction of oxides in the apparatus similar to that described elsewhere [15]. The extracts were subjected to elemental analysis using ICP-OES (Varian ICP-OES Vista-MPX, Varian, Australia).

Specific surface area (Quantachrome Autosorb iQ) and phase composition using X-ray diffraction XRD (Bruker, AXS D8 Advance) were determined for all the oxides. Isoelectric point of oxides (pH_{pzc}) was determined by a slightly modified method proposed by Faria et al. for active carbons [16]. The amounts of electrolyte and oxide were doubled, while the time of pH equilibration was 24 h [6].

Simultaneously, the method accuracy was verified by comparison with mass titration method [6]. No significant differences were observed in pH_{pzc} values. The pH_{pzc} values were determined with an accuracy of 0.15 pH unit.

Ozone in gaseous phase was determined by iodometric method, while ozone in water – by indigo method. Both methods have been described in Standard Methods [17].

2.2. Measurements of ozone decomposition

Experiments in ozone decomposition in water were conducted at room temperature, in high purity unbuffered water (Millipore), whose pH was corrected to 5.0 with hydrochloric acid (10 μM HCl). In each experiment, 200 ml water with appropriate pH was introduced to 250 ml glass reactor. Ozone was produced from pure oxygen using the Crystal ozone generator (Canada). Water was saturated with ozone for 20 min, after the time the concentration of ozone in the aqueous phase was approximately $5.82 \pm 0.64 \text{ mgO}_3/\text{l}$. After switching off the ozonator, a zero sample was immediately taken and 0.5 g of appropriate oxide was introduced. Ozone concentration was measured at specified time intervals. Before each series of experiments, in order to ensure zero demand for ozone, the reactor was saturated with ozone for 20 min. Similar experiments were also done introducing instead of the appropriate oxide, equivalent amount of its aqueous extract. Another set of experiments was carried out in 0.01 M phosphate buffer. All the experiments were repeated three times, in general the precision of ozone determination was better than $\pm 2\%$.

3. Results and discussion

3.1. Characteristics of aluminum oxides

Chemical and physical properties of aluminum oxides used in this study were measured. Table 1 presents the properties of the oxides. The oxides differ in terms of phase composition and specific surface area. The observed pH_{pzc} values are within the range of 7.9–8.8 (non-purified oxides), and following the extraction with water – within the range 7.4–8.8.

In order to identify the contaminants in samples of examined aluminum oxides, qualitative and quantitative analyses of aqueous

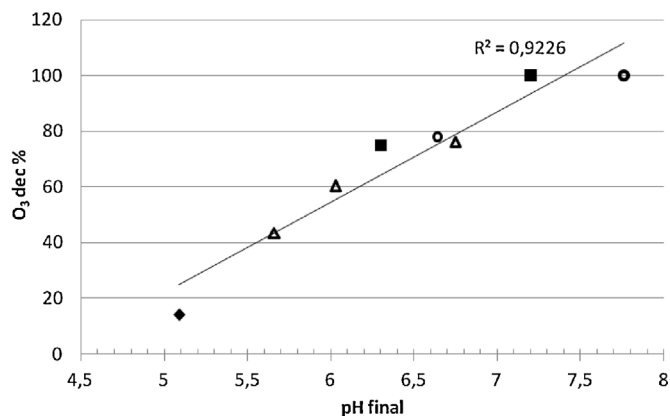


Fig. 1. Relationship between degree of ozone decomposition and pH after introducing different quantities of different aluminas to 200 ml ozone solution with pH 5.0 (adjusted with acid), after 30 min. (◆- O₃; △- SAS (0.5 g; 1 g and 2 g); ■- AA (0.5 g and 1 g); ○-CDO (0.5 g and 1 g)).

extracts of all the oxides were conducted. The results have been listed in Table 2.

Chromium, iron, magnesium and manganese were also found, but in insignificant quantities.

Major contaminant of aluminum oxides is sodium, which constitutes from 77% to over 82% of the total amount of oxide contaminants. This is not surprising as sodium hydroxide is used as the leaching agent in the industrial production of aluminum oxide in the Bayer process [14]. The content of sodium in the studied aluminum oxides ranged from about 13 to over 34 $\mu\text{mol/g}$. Such the amount of sodium easily affects pH after suspension of the oxide in water for e.g. ozone decomposition studies. The increase of pH will be higher when the experiments are carried out at pH close to neutral. It is also worth to emphasize that high purity water used in many research papers does not have any buffer capacity and subsequently is prone to pH changes.

The other elements: Ca, K, Si are also the post-production material and they are the main component of so called “red mud” remaining after the leaching of bauxite ore [14]. In turn, B is characteristic for bauxite rich in this element [18]. However, it is mainly sodium, as alkaline element, that is responsible for the increase in water pH in contact with aluminum oxide and consequently, for ozone decomposition.

3.2. The pH control

In the first experiments, ultrapure water with pH corrected by hydrochloric acid to pH 5.0 was saturated with ozone, different quantities of different aluminum oxides were introduced and disappearance of ozone was observed within 30 min. The rates of ozone disappearance varied for different oxides. Solutions pHs after the process of ozone decomposition were measured and the analysis revealed that pH values also varied and depended not only on the type of oxide but also on its quantity. The dependence between the degree of ozone decomposition and final solution pH was plotted. It turned out that the varied degree of ozone decomposition is highly dependent on pH changes. The results are shown in Fig. 1. The question should be answered what was the reason of pH changes following the introduction of Al_2O_3 to water.

It seems obvious that ozone decomposition after the introduction of aluminum oxides to water was affected by the pH changes and not by catalytic activity of the oxides. Mineral contaminants of aluminum oxides must be considered responsible for the pH changes. Changing the pH of pure water to pH 5.0 requires about 10 $\mu\text{mol/l}$ HCl, while the amount of sodium in oxides can be as high as 35 $\mu\text{mol/g}$ (Table 1).

Table 1

Characteristics of commercially available aluminum oxides used in this study.

Aluminium oxide	BET surface area [m ² /g]	Pore volume [cm ³ /g]	Pore size [nm]	pH _{pzc}	pH _{pzc} after Soxhlet extraction	Crystal phase
AA	335.9	0.41	4.91	8.5	8.0	gamma/alpha
SAS	156.9	4.77	12.16	7.9	7.4	gamma
CDO	214.2	4.57	8.54	8.8	8.8	gamma/alpha

Table 2

Qualitative and quantitative composition of aqueous extracts of the oxides.

Oxide Element	AA [μmol/g]	SAS [μmol/g]	CDO [μmol/g]	Max RSD [%]
Al	6.98	1.96	8.80	±0.88
B	0.10	0.20	0.13	±1.65
Ca	0.02	0.03	0.02	±1.14
K	0.10	0.07	0.18	±2.26
Na	25.04	13.24	34.77	±1.25
Si	0.23	0.55	0.56	±1.67
Total (μmol/g)	32.48	16.08	44.48	

Table 3

Changes in pH during the process of ozone decomposition, after 30 min following the introduction of aluminum oxide (0.5 g oxide per 200 ml water), initial pH corrected using HCl (no buffer added), with 0.01 M buffer (BF). Oxides rinsed with HCl (HCl), extracted in Soxhlet apparatus (S) and aqueous extracts (E).

	Without oxide	AA	SAS	CDO
ΔpH 5.0	−0.03	1.62	0.98	1.84
ΔpH 5.0 (HCl)		0.99	0.22	1.40
ΔpH 5.0 (S)		0.01	0.09	0.80
ΔpH 5.0 (E)		2.68	1.91	3.77
ΔpH 5.0 BF	−0.01	0.23	0.14	0.33
ΔpH 5.0 (E-BF)		0.44	0.24	0.40

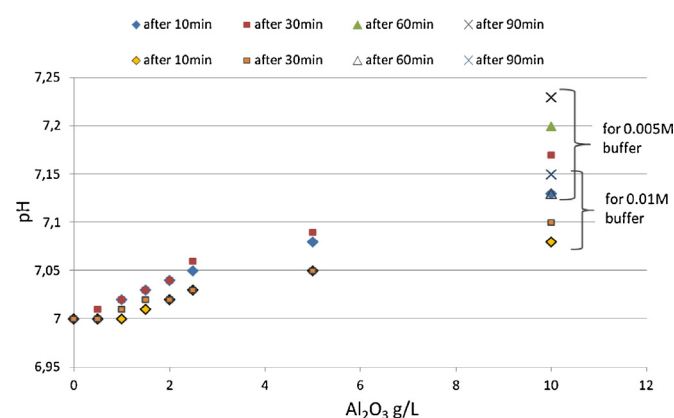
Taking the above into consideration we investigated what pH changes are caused by aluminum oxides introduced to water whose pH was corrected to pH 5.0. Collective results are presented in Table 3. The experiments were repeated 2–4 times each. Although the pH was generally measured with an accuracy of 0.15 pH units the differences in pH values in particular experiments were measured with accuracy better than 0.05 pH unit. The non-purified aluminum oxides caused higher pH increases than purified ones. The highest pH increase was observed for CDO oxide, which contains the highest amount of sodium as the contaminant. The rinsing of oxides with hydrochloric acid slightly reduces their ability to change water pH but it does not eliminate it.

Oxides extracted with water in Soxhlet apparatus are much less effective at increasing pH after being introduced to water, but the ability to change pH is again the strongest for CDO oxide, most contaminated with sodium.

All the oxides were extracted with water in the continuous extractor for 5 hours. Water extracts of these oxides, when introduced to water (in the quantity equivalent to 0.5 g oxide), show the strongest ability to increase water pH. The value of changes in water pH after the introduction of extracts is proportional to the quantity of sodium contaminating the oxide. As results from Tables 2 and 3, mineral contaminants, and especially sodium, are responsible for pH changes in solutions ozonated in the presence of aluminum oxides.

It can be concluded that pH correction of unbuffered solutions subjected to catalytic ozonation is a largely insufficient for pH control. In all the experiments of catalytic ozonation, not only initial pH of solution should be controlled, but also pH during and after the ozonation process. Only strict and restrictive pH control allows for the separation of the actual catalytic effect from the effect caused by pH increase.

Commonly the buffers are used for the pH control. However, using a buffer does not excuse a researcher from controlling pH

**Fig. 2.** Changes in pH of 0.005 M and 0.01 M buffers with the increasing quantities of added aluminum oxide (CDO).

during the experiment. Fig. 2 shows that not all buffers provide pH stabilization during experiments.

The pH increases more with the lower concentration of the buffer and higher concentration of oxide. The pH value is also dependent on Al₂O₃ contact time with water.

Similarly Alvarez et al. [19], during the ozonation of pyruvic acid at pH 2.5, noticed much lower increase in pH when a buffer was used. It should be, however, emphasized that pH correction to pH 2.5 requires larger quantities of acid, so pH increase will be lower in comparison with pH 5.0.

3.3. Aluminum oxide contaminants vs. ozone decomposition

All aluminum oxides: non-purified, purified with HCl, extracted with water and aqueous extracts of the oxides were tried out as ozonation “catalysts”. In 200 ml water at pH 5.0 corrected with hydrochloric acid, 0.5 g of oxide (or extract of related quantity of the oxide) was introduced and decomposition of ozone was observed. The experiments were repeated in 0.01 M phosphate buffer.

Results are presented in Figs. 3–5.

Introduction of aluminum oxide, or its aqueous extract (in the quantity corresponding to 0.5 g oxide), to water in each case causes the increase in solution pH and in consequence the faster decomposition of ozone (Table 3). The rate of ozone decomposition both in pure water (pH 5.0) and 0.01 M phosphate buffer is almost identical. The decomposition of ozone in buffered aqueous extract is also similar.

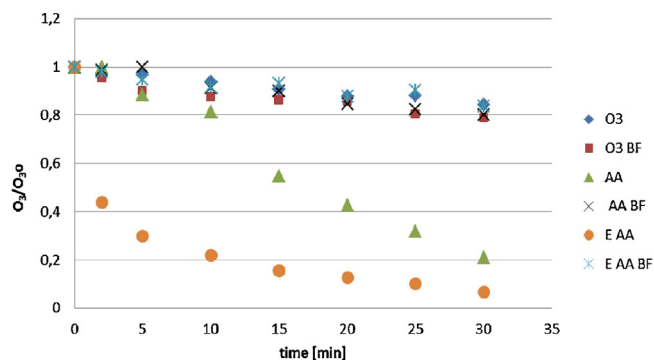


Fig. 3. Influence of 0.5 g AA aluminum oxide and related amount of extract (E) on the process of ozone decomposition in unbuffered water at pH 5.0, and in 0.01 M buffer (BF).

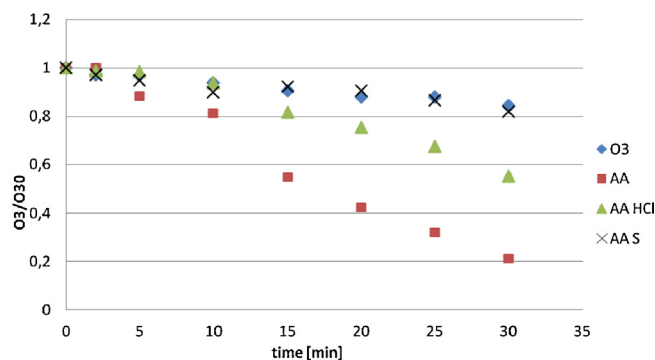


Fig. 6. Impact of AA oxide on ozone decomposition. (0.5 g oxide in 200 ml unbuffered water at pH 5.0) (AA–non-purified oxide, AA HCl–oxide rinsed with acid, AA S–Soxhlet extracted oxide).

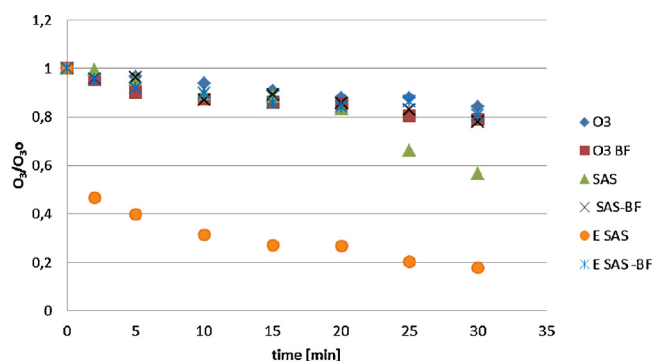


Fig. 4. Influence of 0.5 g SAS aluminum oxide and related amount of extract (E) on the process of ozone decomposition in unbuffered water at pH 5.0, and in 0.01 M buffer (BF).

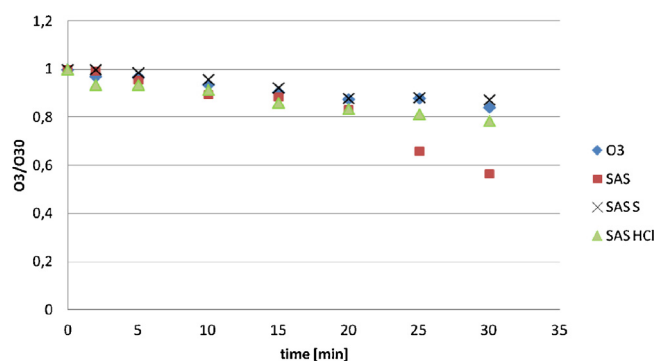


Fig. 7. Impact of SAS oxide on ozone decomposition. (0.5 g oxide in 200 ml unbuffered water at pH 5.0) (SAS–non-purified oxide, SAS HCl–oxide rinsed with acid, SAS S–Soxhlet extracted oxide).

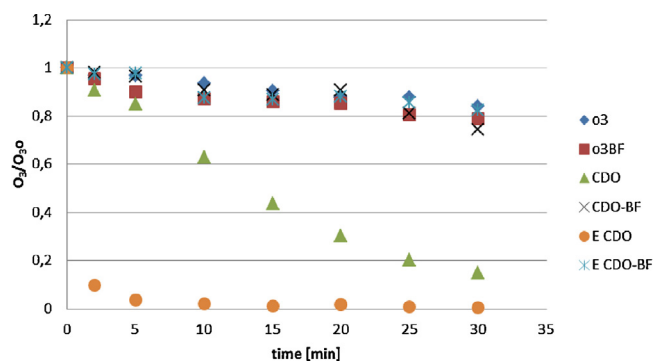


Fig. 5. Influence of 0.5 g CDO aluminum oxide and related amount of extract (E) on the process of ozone decomposition in unbuffered water at pH 5.0, and in 0.01 M buffer (BF).

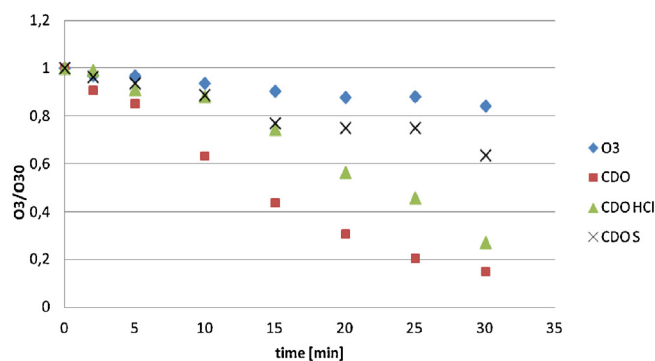


Fig. 8. Impact of CDO oxide on ozone decomposition. (0.5 g oxide in 200 ml unbuffered water at pH 5.0) (CDO–non-purified oxide, CDO HCl–oxide rinsed with acid, CDO S–Soxhlet extracted oxide).

3.4. Do aluminum oxides cause ozone decomposition?

As already mentioned data concerning ozone decomposition are controversial. The previous sections have shown that the addition of buffer during ozone decomposition, in the presence of commercially available aluminum oxides, inhibited the decomposition process. However, in order to definitely confirm the role of post-production contaminants of commercial aluminum oxides, they were subjected to two types of purification. The effect of purification was examined in the decomposition of ozone process. The first series of the oxides was purified by rinsing with 0.1 M HCl, while the other one was extracted with water in Soxhlet apparatus. Catalytic activity of purified oxides was then checked. The results are presented in Figs. 6–8.

As shown in Figs. 6–8, the purification process significantly changes the properties of all commercial aluminum oxides and is related to the removal of alkaline contaminants of these materials. Purification with dissolved acid is not sufficient, the process of ozone decomposition still occurs in the case of CDO and AA, while in the case of SAS ozone decomposition is insignificant, which is connected with the lower content of contaminants in this oxide (Table 2). Extraction with water in Soxhlet apparatus causes the oxides to practically lose their “catalytic” properties, with the exception of CDO. In this case extraction with water was not effective enough to remove all contaminants (Table 3).

Ozone may adsorb on alumina surface but water would strongly prevents such adsorption. First of all ozone is a relatively nonpolar molecule and its hard to believe that it can compete for an

adsorption sites with water molecules [1]. Ozone molecule have some basicity and it would adsorb on Lewis acid sites but again water molecules are much stronger Lewis bases and thus H₂O molecules are much more likely to occupy such sites if available [20]. Roscoe and Abbat [21] have also shown that the adsorption of ozone on the alumina surface is possible but exclusively on a dried surface. It confirms again that the water strongly competes with ozone molecules to the adsorption sites on alumina surface. If the adsorption of ozone on alumina surface is impossible in the prevailing presence of water molecules then catalytic ozone decomposition by the oxide is also impossible.

4. Conclusions

- (a) Pure aluminum oxides are not catalysts of ozone decomposition in water.
- (b) Properties of aluminum oxides are modified by mineral contaminants. The main contaminant of alumina is sodium, which causes pH increase after the introduction of oxide to water. The greatest threat of uncontrolled pH changes concerns solutions at about neutral pH.
- (c) In studies of catalytic ozonation, strict pH control is necessary.
- (d) Using buffer does not excuse the researcher from controlling pH during the studies of catalytic ozonation mechanisms.
- (e) In the processes of catalytic ozonation, attention should be given to catalysts' purity.
- (f) Lack of catalytic ability to decompose ozone does not exclude the ability of alumina to other catalytic activity in e.g. Langmuir-Hinshelwood mechanism or ozone attack on adsorbed organic molecule.

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